

REMARKS

Reconsideration of the patentability of the claims of the instant application, as presented above, is solicited in view of the following remarks.

The examiner's comments concerning the language of the specification and claims have been considered and the instant application text reviewed with the examiner's comments in mind. This review has resulted in applicants submitting a substitute specification herewith. It is believed that the instant substitute specification obviates all of the objections that have been raised by the examiner. This substitute specification does not introduce any prohibited new matter and is therefore enterable. To the extent that the examiner finds that any of his language issues have not been obviated, he is requested to advise application in detail and is asked to suggest rewording where needed. Every effort will be undertaken to accommodate the examiner's suggestions. It is urged that the examiner withdraw these objections.

Note is taken of the examiner's objection to the use of the term "predominantly" in connection with the proportion of magnesia in the instant absorbent material. The examiner's attention is directed to the cited Albers et al. patent that uses this same term in relation to the proportion of this same material. Attention is specifically directed to column 2 line 7 and to many other places in this patent where the same or similar terminology is used. Clearly, the use of this language is acceptable in the art and is known by the art to reflect the desired proportion of magnesia. This term is used in the instant specification and claims in exactly the same manner as has been accepted by the state of the prior art. It is therefore urged that the objection be withdrawn.

The examiner's comments concerning the initially filed declaration have been considered. A newly executed declaration is being filed herewith in order to obviate the objections raised by the examiner. It is urged that the examiner withdraw this objection.

This invention is directed to an improvement in the removal of sulfur values from gas streams containing such sulfur values. It has been disclosed (see the instant cited Albers et al. patent) that sulfur oxides can be extracted from gasses containing the same by contacting such

gasses with a suitable sulfur absorbent material. The cited Albers et al. patent discloses this general process and suggests using hydrotalcite as the sulfur oxide absorbent. Further, this patent discloses using a binder with the hydrotalcite. A whole series of such suggested binders are set forth in column 3. One of the binders that is mentioned, among many, many others is chlorite.

This disclosure might be considered to suggest the use of hydrotalcite bound with chlorite a sulfur oxide absorbent, and, indeed, the Albers et al. reference embraces and discloses such a combination. The instant invention, however, is an improvement over this disclosure. Specifically, this invention absorbs sulfur oxides from a gas stream containing the same by using a high magnesium chlorite as the absorption solid. There are many known materials that are embraced by the name "CHLORITE". If one looks on the internet, one will find literally dozens of "CHLORITES". These have widely varying magnesium content. According to the instant invention, one of the important claimed absorbents is chlorite having a very high magnesia content. This is clearly a subset of the general class of chlorites that are disclosed in the Albers et al. patent. However, it is a subset that would not have been recognized by a person of ordinary skill in this art.

In the Albers et al. patent, chlorites are disclosed as possible binders. There is no disclosure of these materials as sulfur oxide absorbers. Therefore, one of ordinary skill in this art would not associate chlorites with sulfur oxide absorption. More importantly, from the disclosure of the Albers et al. patent, one of ordinary skill in this art would not look to chlorites of any magnesia content (and the chlorite group of minerals has a widely varying magnesia content) as sulfur absorbents. Certainly, there is nothing in this reference to suggest that chlorites of high magnesia content would be especially effective in removing sulfur oxides from gases.

In a second aspect of this invention, it has now been discovered that, for some totally unknown and unexpected reason, sulfur oxide absorbents comprising chlorites have better sulfur oxide removal qualities in second runs as compared to first runs. That is, if an absorbent comprising high magnesia chlorite absorbs a certain amount of sulfur oxides from a gas containing the same in a first pass, once the sulfur oxides have been desorbed from the absorbent (containing high magnesia chlorite) and the regenerated chlorite absorbent is recycled to the absorption side, it unexpectedly absorbs more sulfur oxides (under the same operating conditions) than it did on the

first pass. The data presented in this application fully support that contention, but these data do not shed any light on why this should be so. Again, this is a technique that is not disclosed in any reference and certainly supports patentability whether considered from an anticipation or an obviousness perspective.

It is to be noted that the outstanding action has rejected the patentability of claims 11 and 17 as being anticipated by the disclosure of the Albers et al. reference. These claims have been replaced by the instant new set of claims and none of these new claims is similarly rejectable. Claims 1, 2, 7-9, and 12 have been rejected as being directed to obvious subject matter in consideration of the disclosures of this same reference. For the reasons set forth above, that rejection too does not apply to the claims as now presented. Further, the aspect of this invention that requires an absorbent made up of both a chlorite and a hydrotalcite, and further requires that at least the chlorite component have been presubjected to at least one absorption/desorption cycle is clearly not disclosed in the cited and applied reference.

The examiner has cited the Wright et al. patent, in combination with the disclosure of the Albers et al. patent, as support for a rejection of the patentability of the original claims of this application as being directed to obvious subject matter. This position of the examiner is respectfully traversed. It is noted that the examiner has admitted (see page 9) that the Albers et al. patent does not disclose the solid sorbent materials being claimed herein. He also admits that the Wright et al. patent does not disclose the specific absorbents being claimed herein. However, the examiner asserts that it would have been obvious to combine the disclosures of these two references to make a *prima facie* case of obviousness. That contention is respectfully disagreed with and traversed.

The examiner's expressed opinion is that it would have been obvious for a person of ordinary skill in the art to use the amesite of the Wright et al. patent in the sulfur oxide sorption process disclosed by Albers et al. It is Hornbook law that for some combination of disclosures to be obvious, there must be something in the references to suggest such a combination. Wright et al. discloses the use of phyllosilicate material as cracking catalysts, not as sulfur oxide sorbents. If these two references are to be combined, it would not be by employing amesite as an absorbent, but

by using amesite as a cracking catalyst (that is what is disclosed by Wright et al). In one aspect of the instant invention, sulfur oxide sorbents are employed along with hydrocarbon cracking catalysts. So, the appropriate combination of the disclosures of these two references might be a catalyst comprising hydrotalcite bound with low magnesia chlorite in combination with amesite cracking catalyst. That is not what is being claimed herein. There still would be missing the pretreatment of the chlorite; the use of high magnesia chlorites; the combination of high magnesia chlorites with high magnesia hydrotalcites; or the use of high magnesia hydrotalcites in combination with high magnesia chlorites where the combination has been pretreated by exposure to a gas containing sulfur oxides followed by desorption of the absorbed sulfur oxides.

It is urged that the examiner reconsider all of his rejections in light of the new set of claims that are presented herein. There are clear lines of distinction between what is being claimed and what is disclosed in the prior art. Based on these comments and the newly submitted claims, it is believed that all claims should now be in condition for allowance.

The examiner has entered an obviousness type double patenting rejection of the originally filed claims 11 and 17 over the claims of the Albers et al. patent. This rejection is respectfully traversed. The rejected claims are no longer found in this application, and it has been amply pointed out above that the instant invention is an improvement over the material disclosed in the Albers et al. reference. Therefore, applicants respectfully decline the invitation to file a terminal disclaimer.

As an aside, it is noted that the examiner has continuously referred to the Wright et al. '362 patent. It is believed that the examiner intended to refer to the Wright '602 patent and the outstanding action has been read from this perspective. If applicants are incorrect, and some other reference was intended, it is urged that the examiner so inform the undersigned attorney.

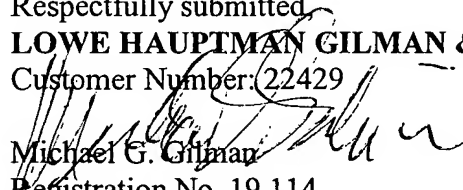
Once again it is urged that the examiner reconsider the content of the outstanding action and withdraw the objections that have been raised and the rejections that have been entered. The subject matter of the Wright et al. patent is not at all material to the patentability of the claims of the instant application. This reference discloses the use of amesite as a cracking catalyst, not as a sulfur oxide absorbent material. In the absence of applicants' disclosure, no one of ordinary skill in this art

would suspect that amesite was especially and unexpectedly exceptionally useful material for absorbing sulfur oxides from a gas containing such. In the absence of an anticipation rejection, therefore, the Wright patent is not a pertinent reference.

The Albers et al reference does not disclose high magnesia chlorites as being especially useful for anything, certainly not sulfur oxide absorption. In fact, the Albers et al. reference does not disclose any chlorite as being useful as a sulfur oxide absorbent. Here too, in the absence of an anticipation rejection, the Albers et al. patent is not a pertinent reference.

The combination of references that the examiner is trying to assemble only is possible from a consideration of the instant specification as a guide and only with the impetus of hind sight. There is nothing in either reference to support the asserted combination.

Therefore, all claims in this application should be allowed.

Respectfully submitted,
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**SUBSTITUTE SPECIFICATION
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TITLE

SULFUR OXIDE SORPTION WITH LAYERED CHLORITE-TYPE CONTACT SOLIDS

FIELD OF THE INVENTION

The present invention relates to chlorite-containing sorbents useful in sulfur abatement.

BACKGROUND OF THE INVENTION

The present invention provides suitable magnesia-rich sorbents for fluidizable catalysts or contact solids, methods for using such materials to reduce the emissions of sulfur compounds from industrial processes, and methods for preparing such contact solids or catalysts. The conversion, processing or burning of sulfur-containing fossil fuels can result in the emission of sulfur-containing compounds, such as H_2S and SO_x , to the atmosphere. To comply with increasingly stringent environmental regulations, materials are sought to reduce the emissions of sulfur compounds from industrial processes. Several methods of desulfurization are currently being used commercially. These methods include flue gas scrubbing as well as various fixed bed, ebullating bed, and fluid bed catalytic reaction processes. Some of these processes treat the flue gas just prior to the release of gas to the atmosphere.

Other processes are performed upstream of the emission release in order to prevent the undesired emission from occurring. The goal of such processes is to reduce emission of sulfur-containing compounds into the atmosphere.

Industry is lacking an economic and effective sorbent composition ~~such as fluidized bed catalyst or additive contact solids~~ for economically removing sulfur oxides from emissions from a variety of industrial processes, such as fluidized bed cracking of heavy petroleum or additive contact solids for use in cold side combustion effluent treatment. Further, the industry lacks effective and economical methods for using a fluidized bed of particles to remove sulfur oxides from emissions.

A structural description of the class of "brucite" crystals is found in the work of Pinnavaia et al (U.S. Patent No 5,358,701, incorporated by reference). Briefly, the metal oxide layers of these crystals consist essentially of magnesium oxide (magnesia, MgO) configured structurally such that it contains ~~with~~ octahedral hydroxy groups. A trivalent metal oxide, such as alumina (Al₂O₃), can be inserted into the brucite crystalline lattice in the octahedrally-coordinated metal oxide layer. Some of these brucitic materials are known as sorbents per se (see U.S. Patent No. 5,928,496). Other brucitic materials are known as binders for sorbent contact solids.

SUMMARY OF THE INVENTION

It has been discovered that magnesia-rich layered phyllosilicates, especially chlorites have sorption properties that are useful for SO_x abatement. Since such phyllosilicate materials are stable in the crystalline oxide structure and essentially reversible in sorbent properties up to about 400°C, stable sorbents may be employed in moderately elevated temperature industrial processes, such as cold side combustion effluent treatment of fossil fuel burning power plants. Natural chlorites containing up to 30 weight percent MgO are known and are useful in this invention, with those containing about 14 to 29 wt% MgO being preferred to be used herein.

In a preferred embodiment of the invention, a novel process of sulfur oxide sorption is provided, wherein a gas containing sulfur oxide is contacted at elevated process temperature ~~at elevated temperature~~, for example from about 200°C up to about 750°C, with a solid phyllosilicate sorbent material to remove sulfur oxide from the gas. A preferred solid phyllosilicate sorbent material comprises crystalline materials having alternating silicate layers and layers having a brucite crystalline structure containing divalent and trivalent metal oxides comprising predominantly magnesia and alumina present in the brucite structure. The amount of phyllosilicate in the solid sorbent can vary from about 10 to 100 wt%. A preferred sorbent composition comprises a mixture of 10 to 90 parts by weight of magnesia-rich chlorite containing about 10-30 weight percent MgO and 10 to 90 parts by weight of hydrotalcite containing at least 50 weight percent MgO. Sulfur oxide sorption and/or desorption may be enhanced by incorporating in the catalyst composition, a solid sorbent material having an effective amount of a metal oxide disposed thereon. Representative metal oxides include cerium, vanadium and platinum in amounts for example of about 50 to 500 ppm.

~~Sulfur oxide sorption and/or release may be enhanced by depositing on solid sorbent material an effective amount (eg 50 to 500 ppm) of metal oxide, such as cerium, vanadium and/or platinum.~~

The invention also provides processes for reducing the amount of SO_x emissions issuing from passing through a fluidized particle bed commercial process, such as (eg FCC fluid catalytic cracking of heavy petroleum fractions refining) or in fossil fuel combustion, such as ~~cold-side~~ coal combustion processes.

DETAILED DESCRIPTION OF THE INVENTION

In the following description, units are given as parts by weight and metric units unless otherwise indicated.

The chlorite group of crystalline materials is often not considered a part of the genus of clays and is sometimes left alone as a separate group within the phyllosilicate structures. It is a relatively large and common group of materials although its members are not especially widely well known. Some of the recognized members of this group of materials include: Amesite, Baileychlore, Chamosite, Clinochlore, Cookeite, Corundophilite, Gonyerite, Nimite, Odinite, Orthochamosite, Penninite, Pannantite, Rhipidolite, (prochlore), Sudoite, and Thuringite. The term chlorite is often used to denote any member of this group when differentiation between the different members is not possible or needed. The general formula is $X_{4-6}Y_2O_{10}(OH, O)_x$. The X represents at least one of either aluminum, iron, lithium, magnesium, manganese, nickel, zinc or sometimes rarely chromium. The Y represents ~~either~~ aluminum, silicon, boron or iron, but usually mostly aluminum/or and silicon.

The gibbsite layers found in conventional clay groups are replaced in the chlorites by a similar layer that is analogous to the oxide brucite. The structure of this group is composed of silicate layers sandwiching a brucite, or a layer similar to brucite, like layer in between, in an s-b-s stacking sequence similar to the above groups. However, in the chlorites, it is believed that there is an extra weakly bonded brucite layer in between the s-b-s sandwiches. This gives the structure an s-b-s b s-b-s b sequence. Variable amounts of water molecules can be disposed between the s-b-s sandwiches and the brucite layers.

Manufacturing Processes

The manufacturing materials and methods useful in practicing this invention are typically disclosed in U.S. Patent No. 5,928,496 (Albers et al) and PCT Publication No. WO 99/19251, both of which are incorporated herein by reference.

The magnesia-rich contact solids made ~~by~~ according to this invention may be self-bound or may include a binder component to hold the inorganic compounds together ~~in~~ into the desired shape, such as spheroidal particles. Depending on the application, different binding systems can be ~~are~~ used, and binders may be added to milled metal oxides/salts prior to forming them into an ~~the~~ aqueous slurry. For example, in more severe high temperature applications, such as fluid cracking catalyst (eg- 700-820°C), a hydrothermally stable inorganic binder such as aluminum chlorohydrate or peptized alumina is preferably used. Effective inorganic binders include sols of aluminum such as aluminum chlorohydrate, peptized aluminas, sols of silica, colloidal silicas, sols of titanium, sols of zirconium clays such as bentonite, calcined kaolinite, kaolinite, metakaolin, montmorillonite, low-magnesia chlorites, talc, and mixtures of these. ~~Desirable~~ Preferred inorganic binders include a sol of aluminum, peptized alumina, a sol of silica, colloidal silica, a sol of titanium, a sol of zirconium, a clay, and mixtures thereof.

Slurry Techniques

Finely-divided milled solids components are mixed with water, preferably containing about 0.1 to 1 wt% surfactant, such as ~~comprising~~ acid stable fluorohydrocarbon, prior to forming and drying the contact solids product of this invention ~~herein~~. It may be advantageous to provide pre-blended, dry-milled materials for dispersion in water which will then be ~~and~~ spray dried or otherwise manufactured into as dry particles in a short time period. Hydrolyzable metal oxides and salts are advantageously pre-blended and stored in the substantial absence of added water. Batch or continuous inline feeding of slurry components is well known. Thereafter, the slurry is pumped or otherwise transported to a ~~the~~ spray dryer feed tank.

It is a significant advantage to use limited amounts of water in forming a fluent slurry for spray drying. By decreasing the amount of water below a weight ratio of 2:1 water:solids (i.e. - typically 30 wt% or more solids), energy savings are realized in the drying step. By maintaining effectively dry (low moisture) solids in admixture before forming the slurring within, for instance one hour before drying, surface hydrolysis is avoided or minimized.

In the preferred methods, a suitable alkaline stable or acid stable surfactant is added to the slurry. Surfactants for improving the physical and catalytic properties of FCC catalysts are disclosed in US Patent 5,330,943 (Shi et al). Improved attrition resistance and standard testing (i.e.- Attrition Index or "AI") are described by Shi et al., who recommend about 0.25-4 grams of surfactant per 5 kg of spray dried product. Preferred acid stable surfactants are fluorohydrocarbons manufactured under

the trade name of DuPont "Zonyl TBS" or of 3M "FC-95", and 0.01-1 wt % of surfactant is satisfactory. The use of surfactant is believed to contribute to attrition resistance by decreasing the advent of "blow holes" during spray drying of the catalyst composition.

Spray Drying

Conventional spray drying techniques are known to the industry, usually withdrawing water from a slurry containing sufficient water to form a fluent mixture of solids and liquid phases, advantageously incorporating a surfactant to impart homogeneity and desirable mechanical properties to the resulting dry products. Heat and low pressure in the spray drying unit permit flashing or rapid evaporation of the liquid phase from a slurry ~~mist~~, resulting in agglomeration of smaller particles to form larger solids, typically having a spheroidal shape and a particles size distribution in the 20-250 micron (μ) range or larger. In the manufacture of FCC catalyst or additive solids, the particles typically have an average size of 20-100 μ . In sorbent particles for fluid bed processes, a larger particle having an average size of about 150-200 μ may be desired.

The phyllosilicate sorbent composition of this invention may include a combination of inorganic oxides with an inorganic binder, an organic binder, or a mixtures of ~~an~~ inorganic and organic binders. Desirable inorganic oxides include a member selected from the group consisting of oxides or hydroxides of aluminum, calcium, cobalt, copper, iron, magnesium, molybdenum, silicon, titanium, vanadium, zinc, tungsten, strontium, nickel, manganese, zirconium, barium, members of the lanthanide series and mixtures thereof. Synthetic hydrotalcites having a large MgO content (preferably about 50-70 wt%) are particularly suitable for use as SO_x sorbents.

The contact solid composition may be self-bound or may include a binder component to hold the inorganic oxide particles together into the desired shape, such as spheroidal particles. Depending on the application, different binding systems are used. For example, in more severe high temperature applications, such as fluid cracking catalyst (e.g.- 700-820 C), a hydrothermally stable inorganic binder such as aluminum chlorohydrate or peptized alumina is preferably used.

Effective inorganic binders include sols of aluminum such as aluminum chlorohydrate, peptized aluminas, sols of silica, colloidal silicas, sols of titanium, sols of zirconium, clays such as bentonite, calcined kaolinite, kaolinite, metakaolin, montmorillonite, chlorite, talc, and mixtures of

these. Desirable inorganic binders include a sol of aluminum, peptized alumina, a sol of silica, colloidal silica, a sol of titanium, a sol of zirconium, a clay, and mixtures thereof.

The smectite clays are especially desirable alone or in combination with zinc oxide/titania mixtures, ~~various inorganic binders and smectite~~. In some applications, such as those that employ a fluidized or ebullating solid catalyst bed, such as those used ~~found~~ in many flue gas desulfurization units, an organic binder such as hydroxypropyl methyl cellulose or polyvinyl alcohol is used.

Other components can be added to the catalyst composition to enhance the performance of conversion catalyst in specific applications or for a specific set of operating conditions. An oxidation promoter such as platinum or cerium can be added to the catalyst solids to facilitate the oxidation of SO_2 to SO_3 , for instance in a ~~the~~ fluid cracking catalyst regenerator, thus improving the overall performance of the catalyst. Desirable additional components can include any number of activators, promoters, oxidizers, reducers, scavengers, and mixtures of these components. These materials may enhance performance. The solid composition preferably is prepared in the form of a spheroidal particle of about 1 to 10,000 microns diameter.

Sorption Process Applications:

~~The present invention provides suitable magnesia-rich sorbents for fluidizable catalysts or contact solids, methods for using such materials to reduce the emissions of sulfur compounds from industrial processes, and methods for preparing such contact solids or catalysts. The conversion, processing or burning of sulfur-containing fossil fuels can result in the emission of sulfur-containing compounds, such as H_2S and SO_x , to the atmosphere. To comply with increasingly stringent environmental regulations, materials are sought to reduce the emissions of sulfur compounds from industrial processes. Several methods of desulfurization are currently being used commercially. These methods include flue gas scrubbing as well as various fixed bed, ebullating bed, and fluid bed catalytic reaction processes. Some of these processes treat the flue gas just prior to the release of gas to the atmosphere.~~

~~Other processes are performed upstream of the emission release in order to prevent the undesired emission from occurring. The goal of such processes is to reduce emission of sulfur-containing compounds into the atmosphere.~~

The inventive process reduces the amount of SO_x emissions emerging from passing through a fluidized particle bed. This process may comprise the step of introducing into the fluid particle bed a microspheroidal catalyst having a composition comprising at least 10 wt% of SO_x-capturing MgO-rich chlorite-type phyllosilicate. Typically, this involves sorbing or capturing SO₃ in the fluid particle bed regenerator as an inorganic sulfate in a fluid cracking catalytic operation. In a petroleum refinery SO_x emissions are often generated in the ~~fluid cracking~~ catalyst regenerator and released in its flue gas.

A typical sulfur abatement process includes the step of introducing into the fluid particle bed a microspheroidal catalyst having a composition comprising at least one SO_x- capturing oxide and at least one inorganic binder. Oxidation of SO₂ to SO₃ can be achieved employing an oxidation promoter catalytic component ~~in a fluid particle bed, such as FCC regenerator.~~

The capture of SO₃ in the ~~fluid particle bed~~ regenerator of an FCC unit as an inorganic sulfate on the SO_x- capturing oxide is usually followed by reducing the inorganic sulfate to a sulfide in a ~~fluid particle bed reactor/stripper.~~ Then, the sulfur can be released as H₂S upon hydrogenolysis or reduction in the stripper. Incorporation of a minor amount of a vanadium oxide component in the contact solids promotes reduction of sulfate during regeneration of the sorbent.

The catalyst composition is desirably formed into a fluidizable particle having an average particle size in the range of about 20μ-300μ that is useful in both conventional fluidized bed and ebullating bed processes. The SO_x-capturing oxide of the invention is desirably a magnesia-rich solid and/or mixed inorganic oxide additive for catalyzing the capture and release of sulfur-containing compounds in the fluid cracking catalyst. This provides refiners with an effective means for reducing ~~fluid cracking catalyst~~ SO_x emissions, especially from an FCC unit regenerator. The invention provides a contact solids or catalyst composition employed as a formed spheroidal catalyst that reduces the emissions of sulfur containing compounds from industrial processes. For example, in the preferred embodiment of the invention, the MgO-rich phyllosilicate captures and thereby removes the sulfur containing species, such as H₂S or SO_x that is present in the gas stream being treated. Advantageously, this invention is employed to reduce emissions of sulfur compounds from a fluid cracking catalyst (FCC) process especially a catalyst regenerator used in conjunction with the fluid bed cracking operation. Particulate solids are added to the FCC unit in the same manner as the conventional cracking catalyst (e.g.- REY zeolite). The magnesia-rich brucitic additive can be introduced separately or together in a mixture with the cracking catalyst. Usually the addition is

accomplished by a pneumatic conveying system to blow the material directly into the FCC catalyst regenerator. The catalyst additive then circulates through the fluid cracking catalyst unit in direct contact and along with the fluid cracking catalyst. The quantity of fluid cracking catalyst additive that is added and which then circulates in the unit is sufficient to effectively reduce the emissions of sulfur containing compounds from the FCC unit, yet it should ~~need~~ not be present in a proportion so large that it deleteriously affects the operation of the cracking process reactions. Fluid cracking catalyst additive level of between about 0.5 and about 10 weight percent of the circulating fluid cracking catalyst inventory is desirable.

Industrial processes for sulfur oxide abatement may be conducted at various temperatures. In the a coal gasification process, the flue gas or hot gas is passed through a fluidized or ebullating bed of catalyst to remove sulfur compounds. Whereas cold side flue gas abatement may be carried out advantageously at about 200° to 400°C, more elevated temperatures in the 400° to 700°C range may be employed. FCC processes may employ the sorbents at 700° to 820°C or higher temperature, as will be understood by the skilled chemical engineer.

Sulfur Oxide Sorption Testing -

A standard test method for measuring such sorption characteristics is thermogravimetric analysis (TgA), wherein a test sample of the crystalline solid material is heated at predetermined rate to 700 C, releasing water of hydration. A gaseous stream containing the sulfur oxide is then contacted with the sample and weight of sorbed material is measured. Regeneration of the sorbent (i.e.- by reduction of sulfate to sulfite) can be effected by passing a hot gas, such as hydrogen over the sample.

In the following examples, various contact solids were tested ~~test~~ by TgA for comparing SO_x sorption in a controlled heating, sorption and regeneration cycle. A standard duPont TgA unit is employed to test samples in the TgA ramp method. The sample is heated at uniform rate to 700° C with a flowing stream of nitrogen through the sample. The sorption cycle employs 3000 ppm SO₂ in a carrier gas stream containing 3 wt% oxygen and balance nitrogen and maintains the sample at predetermined temperature of 700° C for at least 30 minutes during sulfur oxide sorption. Regeneration is performed by hot hydrogen gas flowing over the sample at 650° C.

Typical naturally-occurring minerals having a chlorite structure are given in the following tables.

Table 1 – Amesite

Chemical Formula:	$\text{Mg}_2\text{Al}(\text{SiAl})\text{O}_5(\text{OH})_4$			
Composition:	Molecular Weight = 278.68 gm			
	<u>Magnesium</u>	17.44 %	Mg	28.92 % MgO
	<u>Aluminum</u>	19.36 %	Al	36.59 % Al_2O_3
	<u>Silicon</u>	10.08 %	Si	21.56 % SiO_2
	<u>Hydrogen</u>	1.45 %	H	12.93 % H_2O
	<u>Oxygen</u>	51.67 %	O	
		100.00 %		100.00 % = TOTAL OXIDE
Empirical Formula:	$\text{Mg}_2\text{Al}_2\text{SiO}_5(\text{OH})_4$			

Table 2 – Chamosite

Chamosite	$(\text{Fe}^{++}, \text{Mg}, \text{Fe}^{+++})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH}, \text{O})_8$			
Chemical Formula:				
Composition:	Molecular Weight = 660.15 gm			
	<u>Magnesium</u>	5.52 %	Mg	
	<u>Aluminum</u>	8.17 %	Al	
	<u>Iron</u>	29.61 %	Fe	
	<u>Silicon</u>	12.76 %	Si	
	<u>Hydrogen</u>	0.31 %	H	
	<u>Oxygen</u>	43.63 %	O	
		100.00 %		
Empirical Formula:	$\text{Fe}^{2+}_3\text{Mg}_{1.5}\text{AlFe}^{3+}_{0.5}\text{Si}_3\text{AlO}_{16}(\text{OH})_2$			

Table 3 –Orthochamosite

Chemical Formula:	$(\text{Fe}^{++}, \text{Mg}, \text{Fe}^{+++})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH}, \text{O})_8$			
Composition:	Molecular Weight = 664.18 gm			
	<u>Magnesium</u>	5.49 %	Mg	9.10 % MgO
	<u>Aluminum</u>	8.12 %	Al	15.35 % Al_2O_3
	<u>Iron</u>	29.43 %	Fe	32.45 % FeO / 6.01 % Fe_2O_3
	<u>Silicon</u>	12.69 %	Si	27.14 % SiO_2
	<u>Hydrogen</u>	0.91 %	H	8.14 % H_2O
	<u>Oxygen</u>	43.36 %	O	
		100.00 %		98.19 % = TOTAL OXIDE
Empirical Formula:	$\text{Fe}^{2+}_3\text{Mg}_{1.5}\text{Fe}^{3+}_{0.5}\text{Al}_2\text{Si}_3\text{O}_{12}(\text{OH})_6$			

Table 3 - Clinochlore (kaemmererite)

Chemical Formula:	$(\text{Mg}, \text{Fe}^{++})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$			
Composition:	Molecular Weight = 595.22 gm			
	<u>Magnesium</u>	15.31 %	Mg	25.39 % MgO
	<u>Aluminum</u>	9.07 %	Al	17.13 % Al_2O_3
	<u>Iron</u>	11.73 %	Fe	15.09 % FeO
	<u>Silicon</u>	14.16 %	Si	30.28 % SiO_2
	<u>Hydrogen</u>	1.35 %	H	12.11 % H_2O
	<u>Oxygen</u>	48.38 %	O	

	100.00 %	100.00 % = TOTAL OXIDE
Empirical Formula:	$\text{Mg}_{3.75}\text{Fe}^{2+}_{1.25}\text{Si}_3\text{Al}_2\text{O}_{10}(\text{OH})_8$	

Table 4 -Gonyerite

Composition:	Molecular Weight = 703.49 gm			
	Magnesium	10.36 %	Mg	17.19 % MgO
	Manganese	23.43 %	Mn	30.25 % MnO
	Iron	9.53 %	Fe	13.62 % Fe_2O_3
	Silicon	15.17 %	Si	32.46 % SiO_2
	Hydrogen	0.57 %	H	5.12 % H_2O
	Oxygen	40.94 %	O	
		100.00 %		98.64 % = TOTAL OXIDE

Empirical Formula: $\text{Mg}_3\text{Mn}^{2+}_3\text{Fe}^{3+}_3\text{Si}_{3.8}\text{Fe}^{3+}_{0.2}\text{O}_{14}(\text{OH})_4$

Table 4 - Nimite

Chemical Formula:	$(\text{Ni}, \text{Mg}, \text{Fe}^{++})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$			
Composition:	Molecular Weight = 666.98 gm			
	Magnesium	6.19 %	Mg	10.27 % MgO
	Aluminum	8.09 %	Al	15.29 % Al_2O_3
	Iron	5.86 %	Fe	3.23 % FeO / 4.79 % Fe_2O_3
	Silicon	12.63 %	Si	27.03 % SiO_2
	Nickel	22.88 %	Ni	29.12 % NiO
	Hydrogen	1.16 %	H	10.40 % H_2O
	Oxygen	43.18 %	O	
		100.00 %		100.12 % = TOTAL OXIDE

Empirical Formula: $\text{Ni}_{2.6}\text{Mg}_{1.7}\text{AlFe}^{3+}_{0.4}\text{Fe}^{2+}_{0.3}\text{Si}_3\text{AlO}_{10.3}(\text{OH})_{7.7}$

Table 5 - Sudoite

Chemical Formula:	$\text{Mg}_2(\text{Al}, \text{Fe}^{+++})_3\text{Si}_3\text{AlO}_{10}(\text{OH})_8$			
Composition:	Molecular Weight = 546.77 gm			
	Magnesium	8.45 %	Mg	14.01 % MgO
	Aluminum	19.25 %	Al	36.36 % Al_2O_3
	Iron	3.06 %	Fe	1.31 % FeO / 2.92 % Fe_2O_3
	Silicon	15.41 %	Si	32.97 % SiO_2
	Hydrogen	1.46 %	H	13.01 % H_2O
	Oxygen	52.38 %	O	
		100.00 %		100.59 % = TOTAL OXIDE

Empirical Formula: $\text{Mg}_{1.9}\text{Fe}^{2+}_{0.1}\text{Al}_{2.9}\text{Fe}^{3+}_{0.2}\text{Si}_3\text{AlO}_{10}(\text{OH})_{7.9}$

In addition to the desired chlorite-type materials, magnesia-rich hydrotalcite containing about 50-70% MgO are excellent SO_x sorbents, alone or in combination with other materials. As an example of suitable synthetic HTC (Sasol "PURAL MG 70") is provided, as described in the following Table.

Table 6 - Hydrotalcite -(HTC)

HTC	
Composition:	Magnesium 70.8% MgO

	<u>Aluminum</u>	29.2% Al_2O_3
Surface Area	201. m ² /g	
Particle size	<25 micron	59.2%
	<45 "	92.9%
	<90 "	100%
Size at 50%	21.6 micron	

Bulk Density 0.59g/ml.

Sorption Examples:

Example 1 -

A standard TgA SO_2 sorption test is run with an admixture of 60 parts by weight of Luzenac chlorite (30 wt% MgO) and 40 parts inert solids (Thiele RC-87 kaolin clay), to which is added 12 parts cerium oxide and 2 parts vanadium pentoxide. The test sample had an average particle size of about 2-10 microns. TgA preheat cycle of about 38 minutes reduced the standardized sample from 100 weight units to about 92 units, probably due to dehydration. SO_x sorption at 70 minutes increased the weight of the sample to about 95.5 units, and hot hydrogen desorption further reduced the sample to 89 weight units. The same sample was subjected to a second sorption cycle, which provided increased sorption from the standardized 100 units to about 106 units. Although the mechanism for increased sorption capacity with recycle is not fully understood, it is clearly demonstrated that solid sorbent is regenerated with hot hydrogen and recycled, thereby enhancing sulfur oxide sorption properties

Example 2 -

The above example 1 is repeated with a mixture of 20 parts by weight of the magnesia-rich chlorite, 50 parts of "Pural MG 70" hydrotalcite, 30 parts kaolin, and the same amounts of cerium and vanadium additives. TgA preheat cycle of about 34 minutes reduced the standardized sample from 100 weight units to about 98 units. SO_x sorption at 50 minutes increased the sample to about 114 units, and hot hydrogen desorption further reduced the sample to about 95 weight units. The mixture of two magnesia-rich components appears to have greater SO_x sorption capacity than would be expected from each component acting alone.

Example 3 -

The above example 1 is repeated with a mixture of 60 parts by weight hydrotalcite, 40 parts kaolin, and the same amounts of cerium and vanadium additives. TgA preheat cycle of about 30

minutes reduced the standardized sample weight from 100 weight units to about 95 units. SO_x sorption at 60 minutes increased the sample weight to about 114 units, and hot hydrogen desorption further reduced the sample weight to about 93 weight units.

According to the present invention, it is advantageous to employ solid sorbent material comprising at least one layered magnesia-rich crystalline material containing layers of brucite structure, wherein the brucite material is predominately magnesia, having an average MgO content of at least about 50wt%, particularly wherein the sorbent comprises a mixture of magnesia-rich chlorite and hydrotalcite in a weight ratio of about 10:90 to 90:0 chlorite:hydrotalcite.

While the invention has been shown and described by particular examples, there is no intent to limit the inventive concept except as in the following claims.

CLAIMS:

1. In the process of sulfur oxide sorption wherein a gas containing sulfur oxide is contacted at elevated process temperature with a solid sorbent material to remove sulfur oxide from the gas, the improvement which comprises:
solid sorbent material comprising at least one layered magnesia-rich chlorite-type phyllosilicate having a crystalline structure containing alternating layers of brucite structure and silicate structure.
2. The process of sulfur oxide sorption according to Claim 1 wherein said phyllosilicate contains about 10-30 weight percent magnesium oxide.
3. The process of sulfur oxide sorption according to Claim 1 wherein said solid sorbent material has deposited thereon an effective amount of oxidative metal catalyst.
4. The process of Claim 3 wherein said solid crystalline composition contains cerium oxide and vanadium pentoxide.
5. The process of Claim 3 wherein said phyllosilicate consists essentially of amesite.
6. The process of Claim 1 wherein said solid crystalline composition consists essentially of chlorite containing about 14 to 29 wt% magnesia and hydrotalcite rich in magnesia.
7. In the process of cracking a heavy hydrocarbon feed stock containing sulfur compounds, wherein a gas phase containing sulfur oxide is contacted at process temperature in the range of 700° to 820° C with a solid sorbent material to remove sulfur oxide from the gas; the improvement wherein said solid sorbent material comprises at least one magnesia-rich layered phyllosilicate having alternating silicate and brucite layers.
8. In the process of according to Claim 7 wherein said phyllosilicate contains about 10-30 weight percent magnesium oxide.
9. In the process of Claim 7 wherein said phyllosilicate consists essentially of amesite.

10. In the process of Claim 7 wherein said solid sorbent material contains hydrotalcite consisting predominately of magnesia.

11. In the process of sulfur oxide sorption wherein a gas containing sulfur oxide is contacted at elevated process temperature with a solid sorbent material to remove sulfur oxide from the gas, the improvement which comprises magnesia-rich solid sorbent material containing hydrotalcite consisting predominately of magnesia.

12. A process for sulfur oxide abatement comprising:

contacting a gaseous body containing sulfur oxide at elevated process temperature with a solid sorbent material to remove sulfur oxide from the gas;

said solid sorbent material comprising at least one layered phyllosilicate having alternating silicate and brucite layers and contains about 10-30 weight percent magnesium oxide

13. The process of Claim 12 for sulfur oxide abatement wherein the gaseous body includes a vapor phase in the fluidized bed cracking of hydrocarbons; and wherein sulfur dioxide is formed and then converted at elevated temperature, with solid sorbent material having an oxidation metal to convert sulfur dioxide to sulfur trioxide.

14. The process of Claim 12 for sulfur oxide abatement wherein the solid sorbent is regenerated and recycled, thereby enhancing sulfur oxide sorption properties.

15. A sorbent composition comprising a mixture of 10 to 90 parts by weight of magnesia-rich chlorite containing about 10-30 weight percent MgO and 10 to 90 parts by weight of hydrotalcite containing at least 50 weight percent MgO.

16. A method for making solid sorbent particles containing a mixture of:

(a) a first solid sorbent material comprising at least one layered magnesia-rich chlorite-type phyllosilicate crystalline sheet having a crystalline structure containing alternating layers of brucite structure and silicate structures, and

(b) a second solid material comprising crystalline metal oxide and/or salt compounds ;
comprising the steps of:

admixing particulate solids (a) and (b) to form a dry solids blend of at least two different crystalline solids;

recovering a comminuted solids blend having an average particle size of about 1-5 microns;

forming an aqueous slurry of the comminuted solids blend, wherein the aqueous slurry contains surfactant comprising acid stable fluorohydrocarbon;

drying the aqueous slurry to form agglomerated particles

having an average size range greater than about 20 microns; and

recovering dry agglomerated particles having enhanced attrition resistance and particle size uniformity.

17. In the process of sulfur oxide sorption wherein a gas containing sulfur oxide is contacted at elevated process temperature with a solid sorbent material to remove sulfur oxide from the gas, the improvement which comprises:

solid sorbent material comprising at least one layered magnesia-rich crystalline material having layered brucite structure, wherein the brucite material is predominately magnesia.

18. The process of Claim 17 wherein the sorbent composition comprises a mixture of magnesia-rich chlorite and hydrotalcite in a weight ratio of about 10:90 to 90:0 chlorite:hydrotalcite.

ABSTRACT

Chlorite-like phyllosilicate materials are found useful as SO_x sorbents. A novel process of sulfur oxide sorption is provided utilizing these layered materials as contact solids. Typical industrial applications include sulfur removal from fluid catalyst cracking process, cold-side combustion gas sulfur abatement and cleaner coal gasification.

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